Influence of relaxation time on the lifetime of commercial lithium-ion cells

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HIGHLIGHTS

- A relaxation effect on cell capacity was detected for rest periods (≥ 1 h).
- The influence of rest periods on the lifetime is insignificant.
- A long break is better for the lifetime than many short breaks between each cycle.

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ABSTRACT

The influence of rest periods on the lifetime of lithium-ion cells is investigated. The investigations focus on commercially available cells (type 18650) with a lithium–nickel–manganese–cobalt-dioxide (NMC)/lithium–cobalt-dioxide (LCO) blend and lithium–iron–phosphate (LFP) as cathode material and graphite as anode material. The above test cells are subjected to different cycle tests. Important influence factors in addition to the relaxation time are: the current, the temperature and the state of charge (SOC).

We were able to detect an increase of capacity (e.g. 0.1% of the nominal cell capacity for LFP test cells) after a rest period of 120 min in our measurements, the so called relaxation effect.

Further, the question is answered, whether relaxation affects battery lifetime. This was achieved by cycling cells with and without different rest periods at different temperatures and C-rates with a total of 50 test cells. However, no observable differences between cells with and without rest periods (<2 h) were found. Moreover, experiments with many small breaks or one larger break showed that the duration of one continuous relaxation time is more important for the aging behavior, than the sum of rest periods. In addition, also impedance spectra were evaluated.

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1. Introduction

At the moment, the automotive sector is on the edge of an historic switch from conventional to electric powered drive-trains. Three essential features will decide the success or failure of hybrid electric and electric vehicles (HEV, EV): utilization, cost and lifetime. All three are linked together and influence each other. Thus, just a combination of these properties to an optimum will lead to the gain. Especially, the change of lifetime through utilization is a critical part for the most important component of an electric power train, the lithium-ion battery.

However, numerous factors influence the lifetime of such a system. Whereas, the influence of external factor like temperature

T, current I or state of charge (SOC) are topic of research [1], one parameter is rarely considered so far: relaxation time. It is well known, that the cells of a battery require a certain time to reach a steady state in terms of charge, concentration and temperature. However, this time depends strongly on operation conditions like cell loading or temperature as well as on the cell chemistry. Therefore, this study will investigate relaxation phenomena of commercial 18650 type lithium-ion cells as used in the Tesla Roadster [2] and even more their impact on lifetime under different operation conditions like T, SOC, I. In order to evaluate a potential influence, all cells are tested regularly by means of electrical parameter identification tests as well as by electrochemical impedance spectroscopy (EIS). Also, the effect of a multiplicity of short breaks versus long breaks is analyzed for different break durations. The different break duration, refers to the non-operational periods of the battery during its lifetime. Moreover,

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two different cathode materials – iron phosphate and nickel cobalt manganese – will be investigated in order to observe the influence of the cathode design on relaxation effects.

Three aims of this work can be distinguished: First, the detection of relaxation processes and identification of associated time scales and thus possible references to electrochemical processes. Second, statements about the dependency of lifetime on breaks and a description of these dependencies for the tested operation conditions. Third, possible consequences for the operation of HEVs, especially the interaction of the combustion engine and the battery in order to increase battery lifetime. HEVs are controlled by a given operation strategy and an intelligent algorithm will lead to a significant lifetime extension [3]. In addition, the development of accelerated aging tests by reduced break times is an interesting point. At the moment, cycle life test is accomplished by realistic break times, which can be up to 22 h per day for HEVs. However, the transferability and limit of the approach of shorten non-operational periods in such an accelerated aging test is unknown. Thus, knowledge about the interrelation of shortening and reducing lifetime would yield into significant savings of testing times and consequently costs.

2. Theory of cell degradation and relaxation processes

Various publications can be found about degradation processes in lithium-ion cells. An excellent analysis of the processes, divided into each cell component for all common lithium-ion chemistries is given by Vetter et al. [4]. It is shown that several processes take place at each component, leading to an increase of cell resistance as well as decreasing capacity. The main effects for lithium-ion cells seem to be the SEI [5–7] formation and reformation, electrolyte decomposition as well as corrosion and loss of active material. Various degradation effects on aged cells in HEV applications are investigated in Ref. [8]. Based on aging test data, calendar life and cycle life are investigated by considering resistance and capacity as the corresponding parameters. Moreover, the components are analyzed by multiple analysis techniques. Overall, it is identified that degradation for this case is mainly caused by inactive lithium, which is not available for charge transport anymore.

However, none of these works indicate the influence of relaxation on aging. In general three types of relaxation effects during breaks are conceivable:

I. Structure of a double-layer
II. Local concentration and charge equilibrium
III. Drop of concentration gradient in active material and electrolyte

All three relaxation phenomena start after the disconnection of the external current circuit. Different time constants can be observed similar to the ones of modeling by equivalent circuit models [9]. Whereas, the first process occurs in milliseconds interval, the second and third one can take up to hours as indicated in Fig. 1.

Looking at the different lithium-ion cell types, it is obviously that the intercalation process of ions depends strongly on the material property and structure. The active materials, especial the cathode materials can be divided into three categories regarding to their structure [10].

Cathodes with spinel structure like $LiMn_2O_4$ (LMO) are open from all dimensions and are therefore theoretically easier to access for ions, than olivine structures as $LiFePO_4$ (LFP), where the one-dimensional channels can be blocked during cycling. Therefore, two materials with different structures as well as open circuit voltage (OCV) curves will be used in this work. A second, also simple imaginable influence is given by the applied current
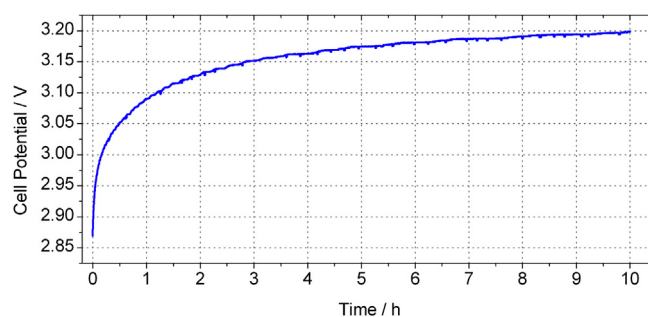

Fig. 1. Measured relaxation of cell voltage (NMC/LCO) after a 1 C discharge step (CCCV), measured at 20 °C.

amplitude and current duration. Evidence for this is given by J. Liu et al. [11]. They have measured the $FePO_4$ phase concentration versus the scan distance along the vertical direction of the electrode at 50% SOC charged at $20\ mA\ g^{-1}$ (0.11 C) and $3\ A\ g^{-1}$ (18 C). These measurements were carried out using a synchrotron X-ray microdiffraction method.

As expected, for low currents a uniform charge balance and for high currents a concentration gradient is found. Thus, a sufficient charge excitation brings the system into an unsteady state, which should be detectable by relaxation processes. A third parameter is given of course by temperature. An equalization of the ions will mostly happen due to diffusion effects, which are strongly temperature dependent. Again, a reference to Fig. 1 is recommended, showing that even after hours no steady state is reached. Another interesting question is the source of relaxation. The simulation carried out by T. F. Fuller et al. [12] gives suggestions about the relaxation dominating electrode. In this simulation sufficient lithium-ion concentration equilibrium is given in the anode already after 6 min. In contrast, no equilibrium is found even after 34 min in the layered cathode. As a consequence, the relaxation periods in this work are placed at fully discharged cells with a SOC of 0% in order to gain a maximum relaxation effect. Additionally, identically tests were carried out with relaxation periods at 100% SOC in order to investigate the effect of the electrodes. The last important parameter is given by the duration of the break. But, not only the duration seems to be important, also the distribution of this duration is very interesting. It is unknown so far, if many short breaks, called micro breaks are more sufficient as few long breaks, called macro breaks for an extension of lifetime. Therefore, the influence of micro breaks versus macro breaks with the same total duration will be investigated and analyzed.

3. Experimental

Experiments were conducted on commercial available 18650 type cells. A 1.1 Ah graphite/lithium–iron–phosphate (LFP) high power cell and a 2.6 Ah graphite/lithium–nickel–manganese–

Table 1
Test cell parameter.

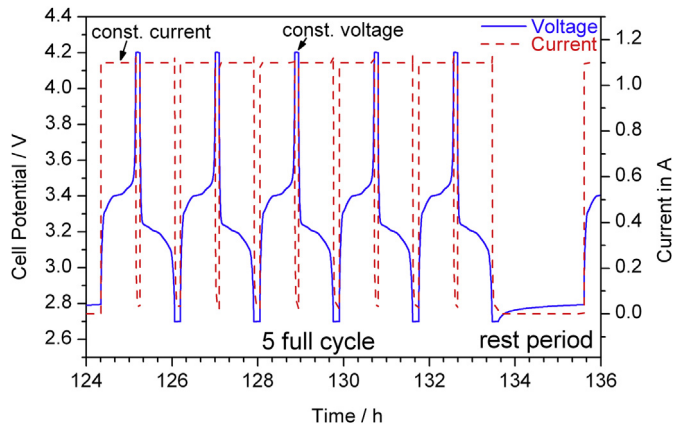|	NMC/LCO type	LFP type
Company	Samsung	A123 Systems
Labeling	ICR-18650-26F	APR-18650-M1A
Dimensions		
Length/mm	65	64.9
Width/mm	18.4	18.2
Electrical parameter		
Capacity/Ah	2.6	1.1
Nominal voltage/V	3.6	3.3
Max. charge voltage/V	4.2	4.2
Discharge cut off/V	2.7	2.7
Operating temperature/°C	−20 to 60	−30 to 60

Fig. 2. Voltage and current vs. time of a LFP test cell cycled with a rest period of 2 h after each five full cycles. This is an example for the measurement program "continues cycling", where each full cycle consists of a constant-current and a constant-voltage step.

Fig. 3. Characteristic Nyquist plot of an EIS measured lithium-ion cell and the used equivalent circuit in this study.

cobalt-dioxide (NMC) and lithium—cobalt-dioxide (LCO) blend, high energy cell were used to investigate the influence of different cell types and cathode materials. The test cell parameters are given in Table 1. The advantages of commercial cells for long term aging experiments are their high repeatability and durability. Therefore, as a drawback, only a two-electrode configuration can be realized for the EIS measurements.

A multichannel test system (Maccor 4000 series) was used for cycle aging of the cells. In the theory part the most important parameters affecting relaxation were described. The cells were cycled or stored at three different temperatures, i.e. 10 °C, 20 °C and 40 °C. The rest period was applied for the majority of the cells in the discharged state (0% SOC) to study the relaxation in a fully lithiated cathode. However, some experiments were also conducted at 100% SOC, so the cathode is delithiated. J. Liu et al. showed impressively how different C-rates affect the polarization respectively the charge carrier distribution in the electrode [11], therefore cells were tested with 1 C and 3 C (where 1 C is the rate at which the full charged cell is discharged in 1 h).

Different parameters were diversified in the measurement program "continues cycling" to investigate their contribution to the relaxation effect. For each full cycle a constant-current/constant-
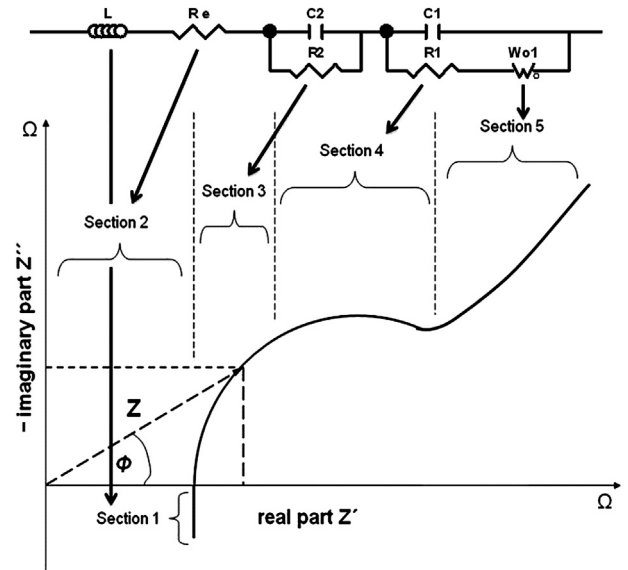
voltage (CCCV) charge/discharge between 2.7 V and 4.2 V, with a cut off current of $I < C_{nom}/20$ for the constant-voltage step (CV) was used (e.g. see Fig. 2). In order to eliminate the influence of the CV step to the capacity development, this period was time limited to the average CV step duration of the first ten cycles.

One group of cells was continuously cycled, whereas other cells were rested for 60 s or 7200 s (2 h) after every fifth full cycle. One pair of cells was stored at the different temperatures, to study the contribution of the calendric aging. Always two cells per experiment were cycled in parallel to avoid cell failures or abnormal degradation.

The question of whether many small breaks between each full cycle (micro break) were as effective as one larger break after five full cycles (macro break) will be answered with the test program "micro vs. macro breaks". One test group will be relaxed for 12 s in the discharged state after each full cycle. The other test group has a 1 min rest step in the discharged state after every fifth full cycle. The investigated parameter matrix is provided in Table 2.

Table 2
Investigated parameter matrix.

Test	Cathode chemistry	Temperature	C-rate	Rest period	SOC at rest
1	LFP	10 °C	1	—	0%
2	LFP	10 °C	1	120 min	0%
3	LFP	20 °C	1	—	0%
4	LFP	20 °C	1	12 s[a]	0%
5	LFP	20 °C	1	1 min	0%
6	LFP	20 °C	1	120 min	0%
7	LFP	20 °C	1	120 min	100%
8	LFP	20 °C	3	—	0%
9	LFP	20 °C	3	120 min	0%
10	LFP	40 °C	1	—	0%
11	LFP	40 °C	1	12 s[a]	0%
12	LFP	40 °C	1	1 min	0%
13	LFP	40 °C	1	120 min	0%
14	NMC/LCO	20 °C	1	—	0%
15	NMC/LCO	20 °C	1	12 s[a]	0%
16	NMC/LCO	20 °C	1	1 min	0%
17	NMC/LCO	20 °C	1	120 min	0%
18	NMC/LCO	20 °C	1	120 min	100%
19	NMC/LCO	40 °C	1	—	0%
20	NMC/LCO	40 °C	1	120 min	0%

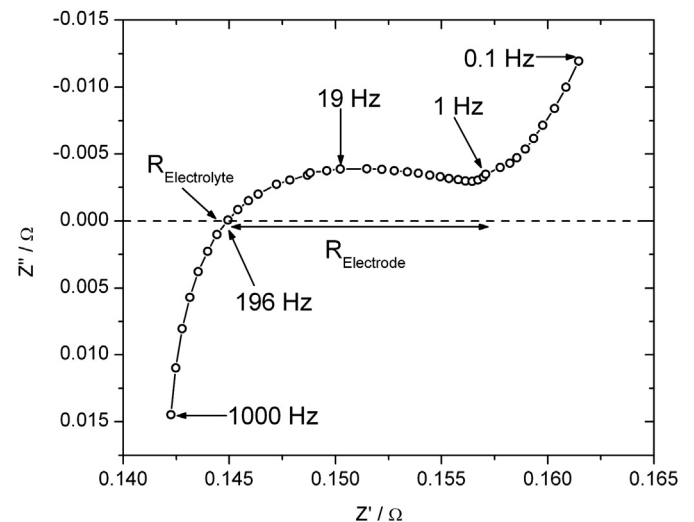[a] Micro break (rest period between each cycle).

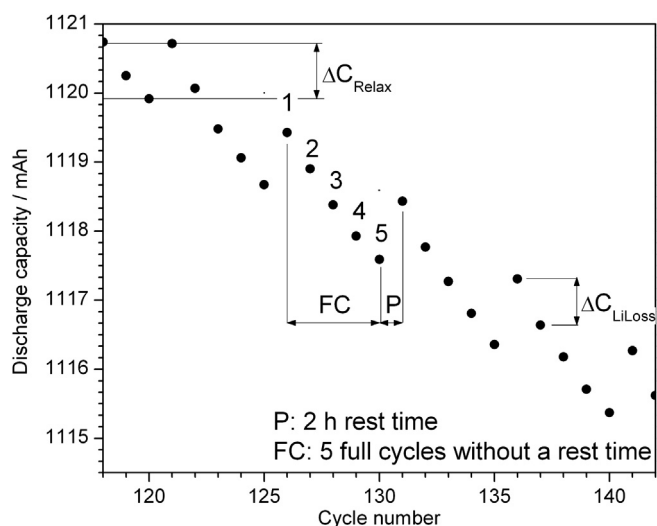**Fig. 4.** Exemplary measured impedance spectrum of a LFP cell.

Fig. 5. Discharge capacity developing of a LFP test cell between the 118th and the 142nd cycle with a two-hour rest period (range P) after five full cycles (range FC) at 40 °C. The capacity difference between the last discharge cycle before and the first discharge cycle after the break is marked with ΔC_{Relax}. The capacity loss from full cycle to full cycle is marked with ΔC_{LiLoss}.

In addition to the electrical parameter tests of the capacity, electrochemical impedance spectroscopy (EIS) is used in this study. This allows a deeper insight in electrochemical process as statements about corresponding time constants and impedances. EIS measurements are state of the art and just a short introduction to the most important points regarding this work is given, more details about EIS in general are given in Refs. [13,14]. The general idea of EIS is to apply a sinusoidal signal at different frequencies and to measure the characteristic cell response. Both methods, to apply galvanostatic a current signal and to measure the voltage response as well as to apply potentiostatic a voltage signal and to measure the current response are possible. However, several study indicated an advantage of the galvanostatic approach for lithium-ion cells [15,16] which is consequently used.

The intermediate EIS measurements of this study were performed by an AC sinusoidal current of 900 mA amplitude in a frequency range from 0.1 Hz to 10 kHz, carried out on an IviumStat System. An ideal spectrum of lithium-ion cells is illustrated in Fig. 3 with the characteristic sections.

Now, these spectra can be reproduced by an appropriate equivalent circuit. The idea of this approach is to analyze the internal processes of the cell by a model as well as to have the opportunity to compare spectra just by characteristic parameters.

A widely used equivalent circuit is shown in Fig. 3 [17,18], representing both electrodes, the electrolyte and the current collectors. Moreover, Fig. 3 indicates the assumed sections of the spectrum and corresponding elements. In relation to the electrochemical processes, the serial resistance R_e represents mainly the ohmic resistance due to the electrolyte, L the inductive influences of the current collectors and wiring, the RC-elements the electrodes and the Warburg element W_0 the charge diffusion in the electrode. However, in practice the time constants of the electrodes are often similar, thus just one semi-circle is observable. An example of this is given by a measured spectrum of the LFP cell in Fig. 4 together with the associated frequencies. Already here, significant different time constants for relaxation are obviously. Whereas, the ohmic resistance and double layer are in a range of 100–300 Hz, diffusion processes just take effect lower than 1 Hz. Now, characteristic parameters can be selected by the program ZView [19] and compared for different operating conditions.

Every second week an EIS was recorded at the cells. The cells were clasp in a special designed holder, in which the positive terminal was supported with a strong spring to ensure a proper electrical connection through the long term cycling. Moreover, the design was optimized to the air circulation in the environmental chambers to ensure a sufficient removal of the thermal waste energy and tempering the cell to the desired temperature.

4. Results and discussion

Two questions were related to our research topic, first which effect has the relaxation during a rest period and second how this affects the lifetime of the cell. In the following part a presentation of the results for the first question is provided.

4.1. Relaxation effect

For the test cells with a two hour rest period between every fifth full cycles, an increase of the discharge capacity was observed which is described e.g. for a LFP test cell cycled at 40 °C in Fig. 5.

After five full cycles an increase in the discharge capacity (ΔC_{Relax}) of 0.8 mAh between the 120th and 121st cycles is detectable in Fig. 5. According to recent literature, the loss of cyclable lithium is identified as the main source of capacity fade [20], therefore the capacity loss from cycle to cycle is called ΔC_{LiLoss}.
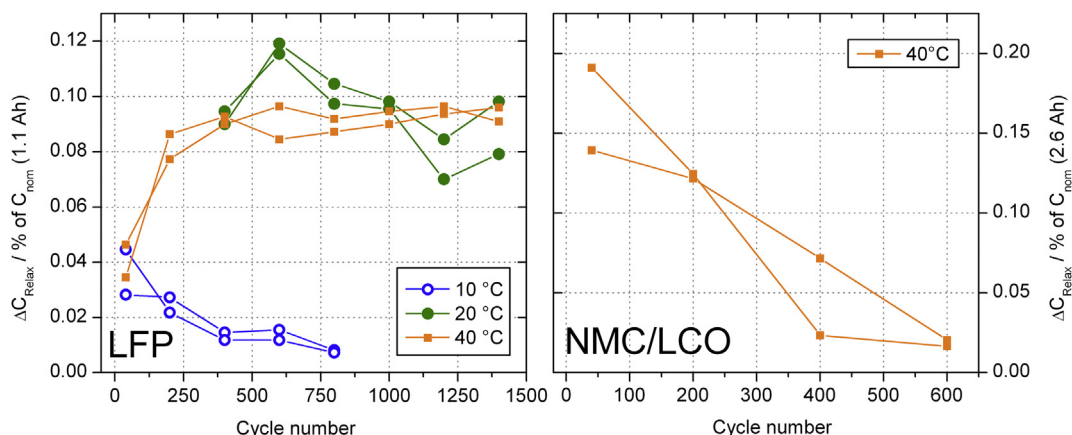

Fig. 6. Development of the ΔC_{Relax} values (two hour rest period between each five full cycles) in percent of the nominal capacity of 1.1 Ah for the LFP test cells (left) and for the NMC/LCO test cells (right) with a nominal capacity of 2.6 Ah for different cycling temperatures.

The capacity of the second cycle after the break, achieved again the value of the capacity before the break.

The influences of the temperature, the duration of the rest periods and the cathode material respectively cell design on the capacity increase after a pause are discussed in the following passage.

The value and the development of ΔC_{Relax} differ from the LFP test cells at 10 °C, 20 °C and 40 °C. An increase of the discharge capacity after a rest period is only observable for a longer duration (as shown here 2 h). A rest period of 1 min between each five full cycles is not sufficient to detect any recognizable capacity increase. The continuous repetition of the relaxation effect is noticeable, therefore the development of the ΔC_{Relax} values in percent of the nominal capacity of 1100 mAh for the LFP test cells are given in Fig. 6. For 20 °C and 40 °C the ΔC_{Relax} values are increasing until reaching asymptotic a plateau. Interestingly the values of ΔC_{Relax} decrease with increasing cycle number for the test group at 10 °C. Between 20 °C and 40 °C there is no discernible difference in the capacity difference, but are significant higher than those of the 10 °C test group, which suggests a kinetically inhibited influence of the lower temperature on the relaxation effect.

At low cycle numbers (<100) ΔC_{Relax} is for 40 °C lower than for higher cycle numbers and no relaxation effect is measurable for the 20 °C test group for cycle numbers lower than 400.

For the NMC/LCO test cells at 20 °C with a rest period of 2 h, the relaxation effect is not observed during the long term cycling; only the test cells at 40 °C show a capacity increase after a 2 h break after each five full cycles. The development of the ΔC_{Relax} value in percent of the nominal capacity of the NMC/LCO commercial cells (2600 mAh) cycled at 40 °C is given in Fig. 6. Starting with the highest value for ΔC_{Relax} at the beginning (four times higher than the values of the 40 °C LFP cells), followed by a steady decrease of the capacity difference over the cycle life it shows a similar behavior to the LFP cells at 10 °C but a contrary behavior to the LFP cells at 20 °C and 40 °C. An explanation for this behavior is found in the development of the discharge capacity over cycle life where these cells are reaching the termination criterion of 80% of the nominal capacity between the 400th and 600th cycle. The aging
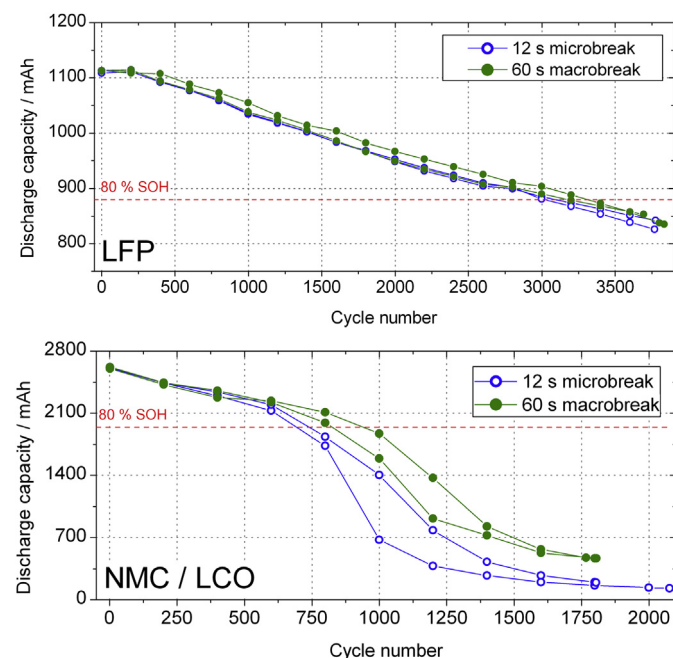

Fig. 8. ΔC_{Relax} values in percent of the nominal capacity of 1100 mAh for a LFP test cell at 20 °C for different relaxation times after five full cycles.

(capacity loss) of the NMC/LCO cells is faster than of the LFP cells (Fig. 7), which means that with increasing cycle numbers the ΔC_{Relax} is covered by the also rising ΔC_{LiLoss}.

Also different relaxation times were tested. The duration of the rest step after five full cycles was altered from 30 s up to five days. The results, presented in Fig. 8, point out, that only after a longer

Fig. 7. Capacity of LFP and NMC/LCO cells with a 12 s micro break between each full cycle and a 1 min macro break between each five full cycles at 20 °C.
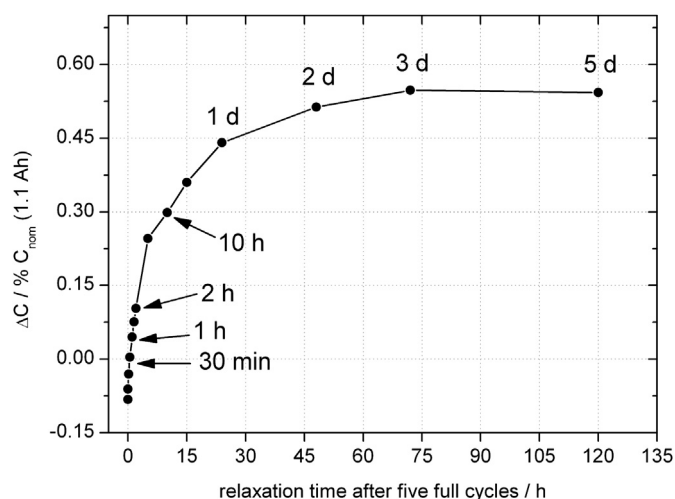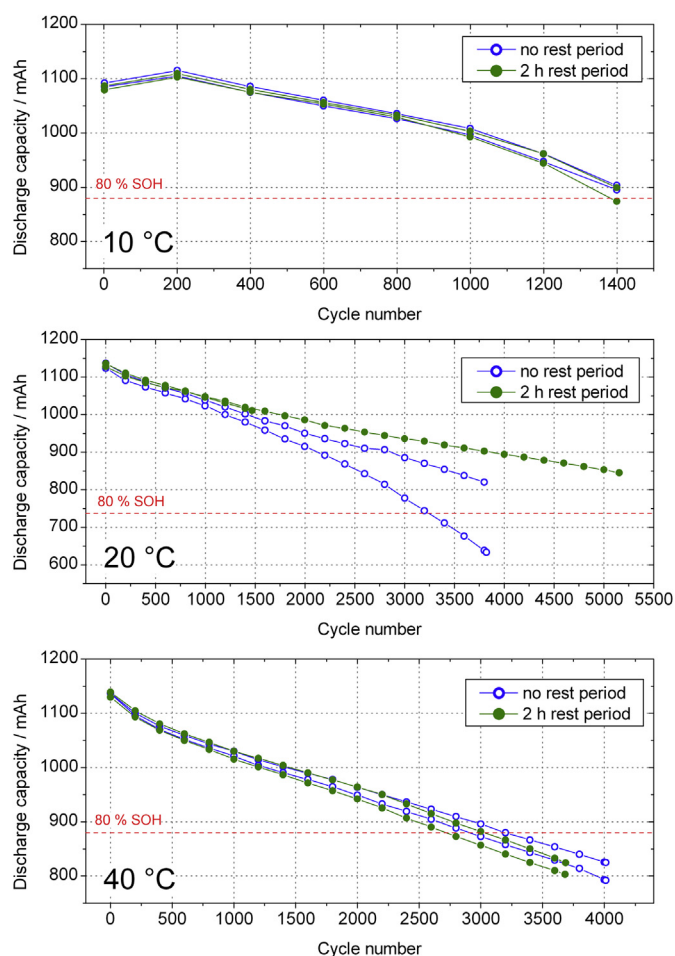

Fig. 9. Capacity of LFP cell with two hour rest period after five cycles and no rest period cycled with 1 C, at 10 °C, 20 °C and 40 °C.
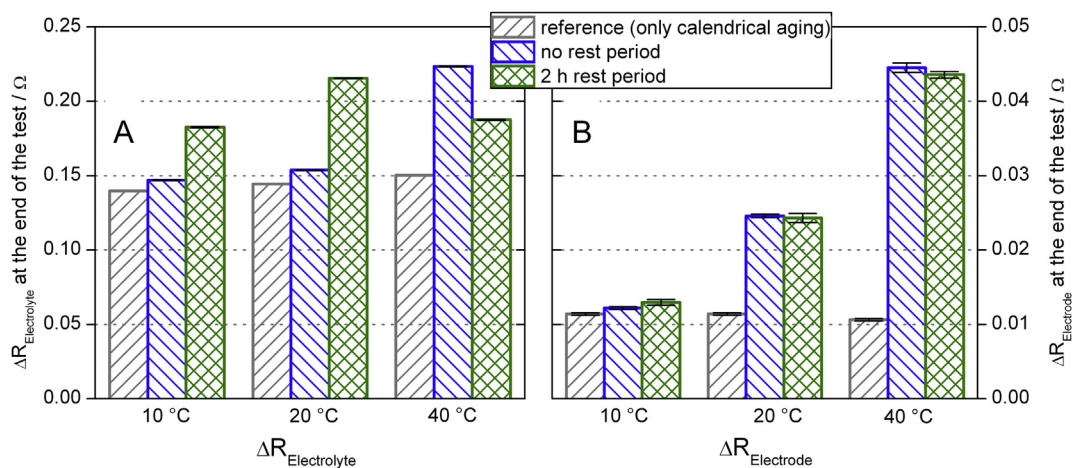
Fig. 10. Change (average value) in the electrolyte resistance (A) and the electrode resistance (B) for each temperature measurement group. The values were obtained from the impedance spectra of the LFP test cells with different rest periods between each five full cycles and the reference cells.

relaxation period, for this cell 30 min, an increase in the discharge capacity is detectable. The differences between the values of ΔC_{Relax} getting smaller with longer relaxation times. Whereas, between 1 h and 1 day is a factor of about ten, just negligible differences for ΔC_{Relax} can be found between three and five days.

To find an explanation for the relaxation effect, the following observations must be considered:

The increase in capacity every break after five complete cycles repeats itself continuously. The discharge capacity of the second cycle after the break, achieved again the value of the discharge capacity before the break, indicating a reversible process that leads to the rise in capacity. The value of the ΔC_{Relax} is changing with increasing number of cycles, which could be due to the influence of aging mechanisms in the cell.

It was shown that the relaxation effect is both temperature and material dependent. The effect occurs in the discharged state of the cell, when the cathode is fully charged, suggesting a mechanism within the cathode. The fact, that the effect occurs only after a longer rest period, speaks for a diffusion process and not for a polarization effect.

Based on our observations, we propose an explanation for the relaxation effect caused by a diffusion mechanism in the cathode material. The lithium-ion transport occurs in olivine structures, like LFP, in one dimensional channel, which can be blocked by structural

defects [21]. An individual active material particle is not a single-crystal but has a polycrystalline configuration. At these intercrystalline boundaries and blocked diffusion channels, lithium-ions can be trapped. However, via kinetically non-preferential diffusion paths the ions can move around these blocked sites. This leads to an explanation based on a temporarily irreversible storage of charge carriers in the cathode. After a long break the ions are again available for cycling, by reducing the load carrier-concentration-gradient and by the relaxation of phase imbalances by kinetically slow diffusion processes.

In addition to the explanation based on the availability of cyclable lithium for the increase of the capacity after a rest period, also a mechanism related to the SEI or electrolyte seems possible. During aging, also in the OCV state, the SEI composition is changing [4]. The internal cell impedance is also affected by the SEI on the anode and so it is possible, that after a long break (e.g. 2 h) the SEI impedance is lower than during or shortly after cycling. A lower impedance is leading to a higher capacity when the same cut off potentials are applied. The same approach is also applicable for an explanation regarding the relaxation effect via changes in the electrolyte during relaxation. On the interface between the cathode and the electrolyte a very fast relaxation of the double layer is expected, similar to the processes in a capacitor. Because the electrolyte has also a major contribution to the internal cell impedance,
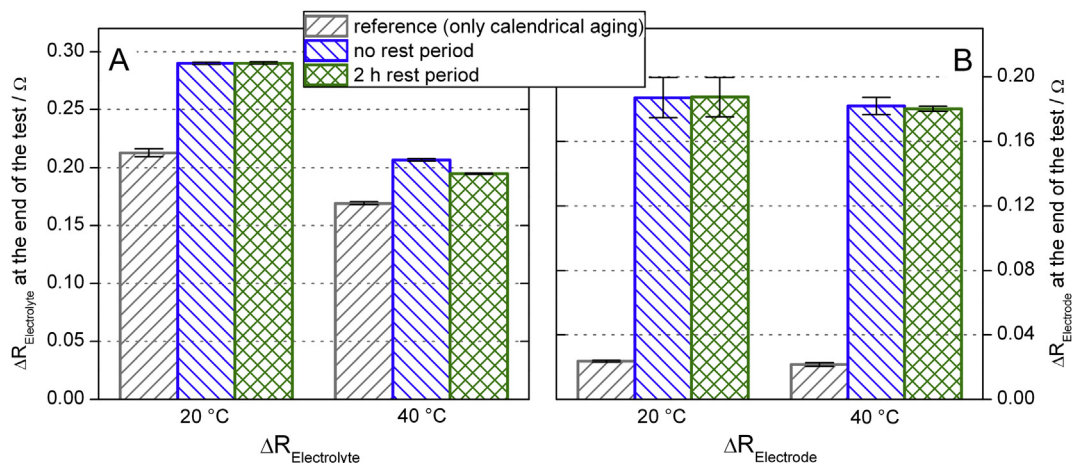

Fig. 11. Change (average value) in the electrolyte resistance (A) and the electrode resistance (B) for each temperature measurement group. The values were obtained from the impedance spectra of the NMC/LCO test cells with different rest periods between each five full cycles and the reference cells.
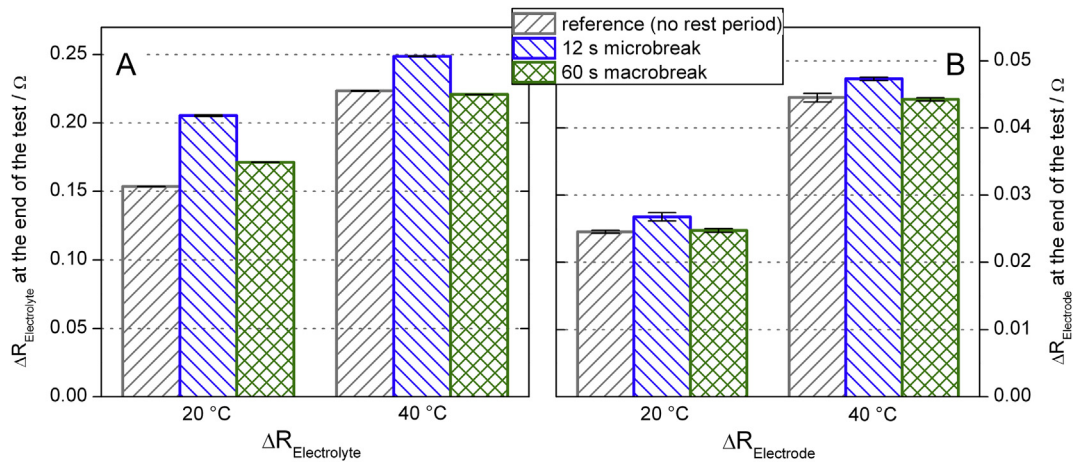
Fig. 12. Change (average value) in the electrolyte resistance (A) and the electrode resistance (B) for each temperature measurement group at the end of the test. The values were obtained from the impedance spectra of the LFP test cells with a macro break between each five full cycles and with a micro break after each full cycle and the reference cells.

it can be suggested that inhomogeneities of the lithium ion concentration distribution [22], in the electrolyte play a major role despite reactions in the double layer. Nevertheless, in order to investigate the mechanism behind the capacity increase further extensive work is necessary and intended.

4.2. Influence of relaxation time on the lifetime of the cells

In the following part the results for the second question will be presented: How the relaxation effect affects the lifetime of a cell?

The development of the discharge capacity for the LFP test cells at 10 °C and 40 °C (Fig. 9) gives no clue if rest periods and the associated relaxation effect increases the life time of the test cells in comparison to the test cells cycled without a rest. Only the cell with a 2 h rest period at 20 °C has a slower capacity fade than the cells without rest step. But this cell presents in comparison with all other LFP cells the best performance, so this result is not representative. In Fig. 10 the values for the electrode (right) and electrolyte (left) resistances at the end of the measurements (end criteria >80% of the nominal cell capacity) are showed. The values for the cells which were only aged by cycling at the different temperatures are nearly the same for all temperature groups, due to the mild temperature range (10 °C—40 °C). The influence of the temperature is clearly visibly for the cycled cells, especially in the electrode resistance. Consistent with the cycling results (Fig. 9) there are only

small differences in the electrode impedance. The electrolyte resistance increases most for the cells with a 2 h rest period at 10 °C and 20 °C. However for the 40 °C cells without rest periods between the full cycles have the highest electrolyte resistance. Probably this is due to the predominant influence of the temperature at 40 °C, since the test cells without breaks were longer exposed to the combination of high ambient temperature and heat generation during cycling than the cells with rest periods.

For the NMC/LCO test cells the results are similar to the LFP cells, where no differences in the discharge capacity development are visible for cells cycled with a rest period between each five full cycles or cycled with no breaks. The increase for the electrolyte resistance is the highest for the 20 °C test group (Fig. 11). Analogous to the LFP test cells, the differences in the electrolyte and electrode impedance between cells with and without a rest period are negligible. Very interesting is the high difference of the electrode resistance between storage and cycling aging, indicating different degradation processes for these cases.

4.3. Micro- vs. macro-breaks

Furthermore, it is investigated if many small breaks between each full cycle (micro break) were as effective as one longer break after five full cycles (macro break). As described in the Experimental section, one test group will be relaxed for 12 s in the
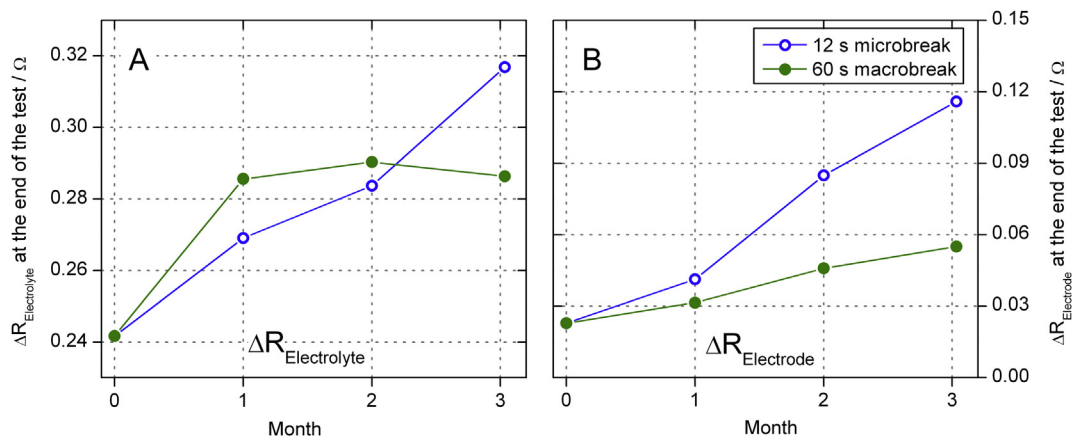

Fig. 13. Monthly change (average value) in the electrolyte resistance (A) and the electrode resistance (B). The values were obtained from the impedance spectra of the NMC/LCO test cells with a macro break between each five full cycles and with a micro break after each full cycle at 20 °C.

discharged state after each full cycle. The other test group has a one minute rest after the discharge step after every fifth full cycle. The development of the discharge capacity for the LFP test cells at 20 °C and 40 °C (Fig. 7) gives no evidence about a faster capacity fade for cells with micro- or macro-breaks. Independent of the rest duration, all cells reach a high number of 3000 full cycles till end of test. The increases of the electrolyte and electrode resistance for the LFP test cells at 20 °C and 40 °C are given in Fig. 12. The cells with a 12 s micro break between each full cycle suffer from a slightly higher impedance raise in the electrolyte as well as in the electrodes than the cells with macro break. Again a difference is observable between the resistance increase for the electrodes between 20 °C and 40 °C, showing the strong influence of temperature on the electrodes.

Micro vs. macro breaks were tested with the NMC/LCO test cells only at 20 °C. In Fig. 7 (bottom) a clear trend is visible: The discharge capacity is declining faster for the cells with a micro break between each full cycle than for the cells with a macro break between each fifth full cycle. The same trend is also found in the development of the electrolyte and electrode resistance of Fig. 13, where the electrode impedance is increasing faster for the micro break than for the macro break test cells.

In summary it is shown, that many short breaks (n) between each full cycle decrease slightly faster in capacity in comparison to one longer break ($t_{macrobreak} = n \cdot t_{microbreak}$).

Combining this result with the conclusion, that the relaxation effect is strongly depended on the duration of the break (Fig. 8), underlines the previous assumption of a diffusion based mechanism (either in the electrode or in the electrolyte) behind the relaxation effect.

4.4. Influence of state of charge and current

As mentioned in the theory part, an influence of the electrode material as well of the cell state of charge (SOC) is assumed for the relaxation behavior. The development of the discharge capacity for the LFP test cells (left) and the NMC/LCO test cells (right) is given in
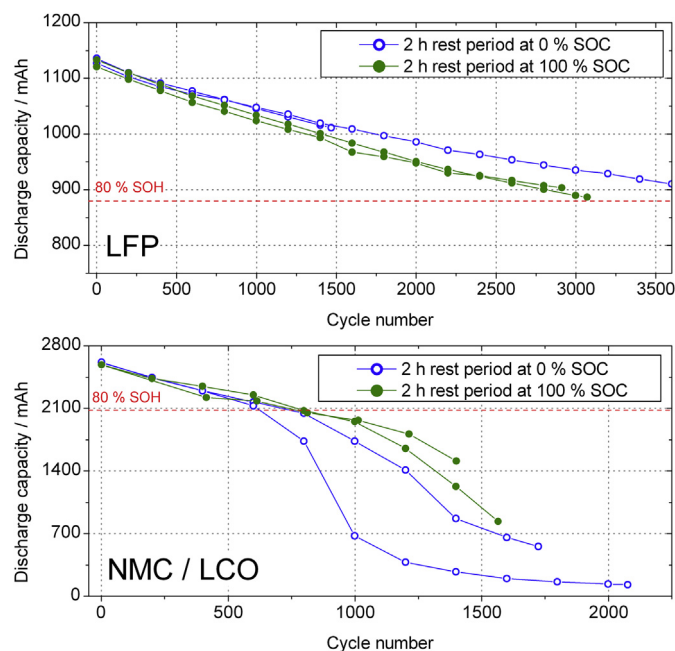

Fig. 14. Capacity of the LFP test cells (top) and the NMC/LCO test cells (bottom) with a two hour rest period in the charged (100% SOC) and discharged (0% SOC) state between each five full cycles at 20 °C.
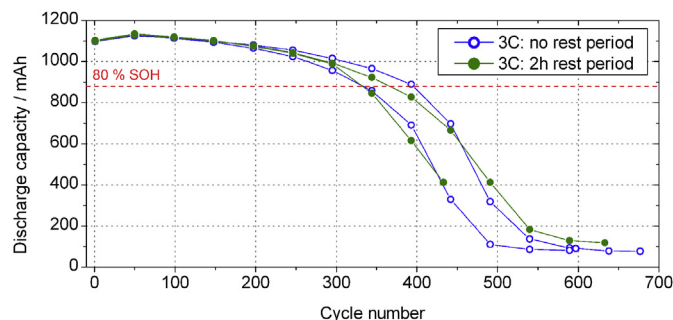

Fig. 15. Capacity of the LFP test cells with a two hour rest period between each five full cycles and no rest period between the cycles at 20 °C with a discharge and charge current of 3.3 A (3 C); the maximum value for the C-rate is 5 C (charge) according to the data sheet.

Fig. 14. There is no large difference for the capacity fade behavior, if the rest period is applied after a charge step (100% SOC; fully lithiated anode) or after a discharge step (0% SOC; fully lithiated cathode). As mentioned before, the cell with the rest period after a discharge step has the best performance of all LFP cells. The influence of the C-rate on the LFP test cells was investigated in Fig. 15. The prevail effect of a higher applied charge- and discharge-current is obviously and superimpose any possible relaxation effect related to a higher cell polarization. Noticeable is the strong effect of the applied current on the achievable cycle number. Whereas excellent >3000 cycles are possible at 1 C, just a tenth can be obtained at 3 C. This is especially interesting since the tests were accomplished at 20 °C. Even at 3 C no significant temperature increase is expected, thus the faster degradation seems to be mainly due to the current instead of thermal processes. Metallic lithium plating and subsequent electrolyte decomposition by the metallic lithium leads to an elevated capacity fade. This effect is also enhanced by high cycling rates [4].

5. Summary

During the last section the influence of relaxation time on the lifetime of commercial lithium ion cells (type 18650) was presented. In fact a relaxation effect on cell capacity was detected e.g. for a rest period of 2 h for the NMC/LCO blend as well as the LFP cathode material. In our best knowledge, this effect was not presented in literature so far. Whereas the overall discharge capacity increases by just 0.10% of the cell capacity at 40 °C for the test group LFP cells, the NMC/LCO cells show a capacity increase of 0.18% at the beginning. For both chemistries the second cycle after the rest period reaches again the value of the capacity before the break.

Surprisingly, the capacity increase ΔC_{Relax} depends strongly on the number of cycles. For LFP cells at 20 °C and 40 °C, ΔC_{Relax} rises with cycling degradation and reaches a plateau after 600 cycles. In contrast, the capacity increase ΔC_{Relax} of the LFP cells at 10 °C and the NMC/LCO cells decreases with growing cycle number.

Based on these observations, two approaches to explain the relaxation process are given. One based on a mechanism in the cathode material and the second one deals with changes in the internal cell impedance, either due to changes in the SEI or in the electrolyte, during the relaxation period.

Furthermore, the question is answered, if relaxation affects battery lifetime. Therefore cells were cycled with and without different rest periods after every fifth full cycles at diverse temperatures and C-rates. However, no observable differences between cells with and without rest periods (≤2 h) were found. Also the evaluation of the impedance spectra showed no significant influence on the electrode or electrolyte resistance. In addition, no differences in discharge capacity were detected for rest periods after a

charge step (100% SOC; fully lithiated anode) and after a discharge step (0% SOC; fully lithiated cathode). Besides, the influence of the C-rate was investigated on the LFP test cells. The prevail effect of a higher applied charge- and discharge-current is obviously and superimpose any possible relaxation effect related to a higher cell polarization.

Moreover, it was investigated whether many small breaks (micro breaks) are as effective as one large break (macro break). For the cells with a micro breaks the capacity is declining faster and the electrode impedance is increasing more rapidly. Therefore, rather the duration of one continuous relaxation time is important for the aging behavior, than the sum of rest periods.

Based on these results, two mayor consequences can be given. First, there is a significant and measurable relaxation effect. Second, no influence of rest periods ($\leq$2 h) was found for both cell types under various operation conditions. Moreover, the very high impact of the current should be deeper investigated and considered.

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